Simple Route to Gradient Concentric Metal and Metal Oxide Rings

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The use of spontaneous self-assembly as a lithography- and external fields-free means to construct well-ordered, often intriguing structures has received much attention as a result of the ease of producing complex structures with small feature sizes. Self-assembly via irreversible solvent evaporation of a droplet containing nonvolatile solutes (polymers, nanoparticles, and colloids) represents one such case.1—6 Recently, self-organized gradient concentric ring patterns have been produced by constraining a drop of polymer solution in a confined geometry composed of either two cylindrical mica surfaces placed at a right angle to one another or a sphere on a flat surface.7—9 Rather than allowing the solvent to evaporate over the entire droplet area as in the traditional approach, in which droplets evaporate from a single surface,1—3 the evaporation is restricted at the droplet edges.7—9 The concentric rings are formed by controlled, repetitive pinning and depinning of the contact line (i.e., “stick−slip” motion).7—9

Ring structures have some unique features compared to their linear counterpart of the same size. For example, persistent currents can be induced by magnetic fields in conducting rings.10 The ability to produce ring structures consisting of metals has been demonstrated on many occasions. Mesoscopic gold rings have been prepared via filling the porous membrane with a solution of gold precursor followed by calcination.10,11 Highly ordered honeycomb-structured gold nanoparticle films with both circular and elliptic pores have been fabricated in the presence of moist air flowing across the surface of the solution.12 However, to the best of our knowledge, no well-ordered concentric rings (i.e., multi-rings) based on metal and metal oxide have been reported. The rings organized in a concentric mode many offer possibilities for many applications, including annular Bragg resonators for advanced optical communications systems.13

Herein, we report on a simple route to concentric rings of metals or metal oxide. The gradient concentric polymer rings with unprecedented regularity were self-organized on metal-(or metal oxide-) coated Si substrate via the evaporation-induced dynamic self-assembly of polymer in a confined geometry (Figure 1a). Subsequently, the rings were utilized as templates for the preparation of ordered metal or metal oxide rings by removing metal or metal oxide between polymer rings, followed by eliminating polymer rings as depicted in Figure 2. This method is fast and cost-effective, dispensing with the need for lithography and external electric fields. Moreover, there is no restriction on metal and metal oxide materials that can be used for the formation of concentric rings.

A thick layer of gold (Au; 45 nm), aluminum (Al; 1 μm), or titania (TiO2; 140 nm) was thermally deposited on Si substrates. To ensure good adhesion between Au (or Al) and Si, a 2-nm-thick TiO2 was first evaporated on Si substrates. To construct a sphere-on-Si geometry inside a chamber, a spherical lens made from fused silica with a radius of ~1 cm and an abovementioned metal- (or metal oxide-) coated Si were used. Both the sphere and Si were firmly fixed at the top and the bottom of sample holders in the chamber, respectively. To implement a confined geometry, an inchworm motor with a step motion of a few micrometers was used to place the upper sphere into contact with the lower stationary Si substrate. Before they contacted (i.e., separated by approximately a few hundred micrometers apart), 23 μL of poly(methyl methacrylate) (PMMA; number average molecular weight, Mₐ = 534 kg/mol, and polydispersity, PDI = 1.57) in toluene solution (c = 0.25 mg/mL on Au-coated Si and c = 1.0 mg/mL on Al- and TiO₂-coated Si) was loaded and trapped within the gap between the sphere and Si as a result of the capillary force. The sphere was finally brought into contact with Si substrate by the inchworm motor such that a capillary-held PMMA solution forms with evaporation rate highest at the extremity as schematically illustrated in Figure 1a.

The evaporation of toluene at the capillary edge simply triggered the pinning of the contact line (i.e., “stick” and forming the first ring).1 This led to an outward flow that carried nonvolatile PMMA to the edge.1 During the deposition of PMMA, the initial contact angle of the capillary edge decreased gradually due to the evaporative volume loss of toluene to a critical angle at which the capillary force (depinning force) becomes larger than the pinning force.8 This caused the jump of the contact line (i.e., “slip”) to a new position at which a new ring developed.3,8,9 Repetitive deposition and recession cycles of the contact line in the sphere-on-Si geometry resulted in the formation of periodic rings.

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It is noteworthy that to form a periodic family of concentric rings of PMMA, the solvent evaporation must be homogeneous. The periodic organization of PMMA rings makes them a powerful template for producing metal and metal oxide rings as schematically illustrated in Figure 2. PMMA rings formed at the surface of metal- or metal oxide-coated Si (Figure 2b) were treated with a selective solution to remove the metal or metal oxide layer between PMMA rings (Figure 2c). Subsequently, the sample was rinsed with acetone thoroughly to remove PMMA, thereby exposing underlying metal or metal oxide (Figure 2d), replicating the gradient feature of PMMA rings in terms of \( \lambda_{C-C} \). The optical micrographs of PMMA rings on the Au-coated Si surface, PMMA rings after treatment with KI/I\(_2\) mixed solution to remove Au between adjacent rings, and Au rings formed (i.e., exposed) after final removal of PMMA on their top with excessive acetone are shown in Figure 1b (left panel), Figure 1c, and Figure 1d, respectively. The order of Au rings (Figure 1d) was reminiscent of the arrangement of PMMA rings (left panel in Figure 1b) and was not disrupted during the successive eliminations of Au and PMMA (Figure 1c,d).

To verify the accessibility of the sequence demonstrated in optical micrographs (Figure 1b–d; corresponding to the steps in Figure 2b–d), atomic force microscopy (AFM) measurements were performed. Figure 3 shows three-dimensional (3D) AFM height images (left) and the corresponding cross sections taken perpendicular to the rings (right). Locally, the rings appeared as the stripes. The optical micrographs of rings (i.e., stripes locally; left) and corresponding profiles (right). (a) PMMA rings formed on a Au-coated Si surface via controlled, repetitive “stick–slip” motion of the contact line (\( c = 0.25 \text{ mg/mL} \)). (b) PMMA rings after removal of Au between adjacent PMMA rings with KI/I\(_2\) mixed solution. (c) Au rings obtained after completely rinsing PMMA off with excessive acetone. These images correspond to the stages shown in Figure 1b–d, respectively. The image size is 100 × 100 \( \mu \text{m}^2 \).

The periodic organization of PMMA rings makes them an intriguing template for producing metal and metal oxide rings as schematically illustrated in Figure 2. PMMA rings formed at the surface of metal- or metal oxide-coated Si (Figure 2b) were treated with a selective solution to remove the metal or metal oxide layer between PMMA rings (Figure 2c). Subsequently, the sample was rinsed with acetone thoroughly to remove PMMA, thereby exposing underlying metal or metal oxide (Figure 2d), replicating the gradient feature of PMMA rings in terms of \( \lambda_{C-C} \). The optical micrographs of PMMA rings on the Au-coated Si surface, PMMA rings after treatment with KI/I\(_2\) mixed solution to remove Au between adjacent rings, and Au rings formed (i.e., exposed) after final removal of PMMA on their top with excessive acetone are shown in Figure 1b (left panel), Figure 1c, and Figure 1d, respectively. The order of Au rings (Figure 1d) was reminiscent of the arrangement of PMMA rings (left panel in Figure 1b) and was not disrupted during the successive eliminations of Au and PMMA (Figure 1c,d).

The gradient concentric Au sample was then reacted with 25 \( \mu \text{L} \) of 6-FAM-Q-labeled (green emitting fluorescent dye; 6-FAM-Q: 1-dimethoxytrityloxy-3-[O-(N-carboxy-di-O-pivaloyl-fluorescein)-3-aminopropyl]-propyl-2-O-succinoyl-long chain alkylamino-CPG) thiolated oligonucleotides (pur-
A larger $\lambda_{c-C}$ is clearly evident due to the use of the PMMA toluene solution with a higher concentration ($c = 1$ mg/mL; Figure 5) as compared to the 0.25 mg/mL solution used for preparing Au rings (Figure 1b–d). The height of the rings is mainly dictated by the thickness of the metal and semiconductor sputtered on the Si substrates prior to drying-mediated self-assembly of PMMA rings as seen in Au and TiO$_2$ rings, possessing a smooth ring surface (Figure 3c and the inset in Figure 5b). However, in the first step of preparation of Al rings, due to fast reaction of Al and KOH, Al between the PMMA rings (see schematic in Figure 2b,c) was removed very quickly. In the meantime, partial dissolution of intact Al underneath PMMA rings occurred, thereby reducing the width and the height of intact Al. Consequently, humplike Al rings were obtained (inset in Figure 5a).

In conclusion, a rational construction of simple sphere-on-flat geometry provides remarkable control and flexibility over the preparation of gradient concentric rings of non-volatile solutes produced by repeated “stick-slip” motion of the contact line. This simple, lithography-free route allows subsequent preparation of a great variety of metal and metal oxide concentric ring patterns with controlled spacing, size, and thickness. The utilization of such a gradient replica to engineer biopolymers (i.e., oligonucleotides) has been demonstrated. We envision that, owing to intrinsic gradient nature in spacing and width together with well-controlled physical and chemical surface properties, metal and metal oxide rings may provide the basis for combinatorial study of dewetting of polymer thin films, phase separation of polymer blends as well as polymer/liquid crystal mixtures, and long range ordering of block copolymers to explore finite size (i.e., confinement) effects in one step. These rings may also be employed as unique surfaces for studying the confinement of transmembrane cell receptors and the biological recognition process.

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Figure 4. Fluorescence image of 6-FAM-Q-labeled thiolated oligonucleotide patterns formed on Au rings. The scale bar is 100 μm.

Figure 5. Optical micrographs of gradient concentric rings of (a) Al and (b) TiO$_2$. The scale bar is 20 μm in part a and 50 μm in part b, respectively. Representative 3D AFM images (80 × 80 μm$^2$) are given as insets. The z scale is 1 μm in part a and 400 nm in part b. The concentration of PMMA toluene solution used to produce PMMA rings is $c = 1$ mg/mL. The oligonucleotide-deposited Au surface was rinsed with DI water to wash away unbonded oligonucleotide. The thickness of oligonucleotide adsorbed on Au rings was 7 nm, determined by AFM. The oligonucleotides adsorbed physically on Si surfaces (between Au rings) also caused fluorescence but were much weaker. In the future, an extensive rinse with a phosphate-buffered solution will be conducted, and the pH of the solution and the rinsing time will be optimized to achieve a clear fluorescence image exclusively on the Au rings.

To demonstrate that a wide variety of metals or metal oxides can be used to make rings in gradient concentric mode, Al and TiO$_2$ (semiconductor) coated Si substrates were employed. TiO$_2$ possesses the highest known dielectric constant of the oxide materials that renders a variety of applications in electronics, optics, and solar cells.

Figure 5 shows optical micrographs of Al rings and TiO$_2$ rings created in a manner similar to the process of preparing Au rings. Al and TiO$_2$ between PMMA rings were selectively removed with 20 wt % potassium hydroxide (KOH) DI water solution for 2 min and 5 vol % hydrofluoric acid (HF) DI water solution for less than 1 min, respectively. Finally, PMMA rings were completely rinsed off with acetone, thereby exposing Al and TiO$_2$ underneath. The heights of the Al and TiO$_2$ rings are 410 and 140 nm shown in Figure 5a,b, respectively. Representative 3D AFM height images are shown in Figure 5a,b as insets, respectively. The $\lambda_{c-C}$ of the metal and semiconductor rings can be easily tuned by varying the concentration of the PMMA toluene solution. A larger $\lambda_{c-C}$ is clearly evident due to the use of the PMMA toluene solution with a higher concentration ($c = 1$ mg/mL; Figure 5) as compared to the 0.25 mg/mL solution used for preparing Au rings (Figure 1b–d). The height of the rings is mainly dictated by the thickness of the metal and semiconductor sputtered on the Si substrates prior to drying-mediated self-assembly of PMMA rings as seen in Au and TiO$_2$ rings, possessing a smooth ring surface (Figure 3c and the inset in Figure 5b). However, in the first step of preparation of Al rings, due to fast reaction of Al and KOH, Al between the PMMA rings (see schematic in Figure 2b,c) was removed very quickly. In the meantime, partial dissolution of intact Al underneath PMMA rings occurred, thereby reducing the width and the height of intact Al. Consequently, humplike Al rings were obtained (inset in Figure 5a).

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